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Alternative N precursors and Mg doped GaN grown by MOVPE

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Abstract

In this paper, we address two different aspects relevant to the growth of GaN. The first part concerns alternative nitrogen source whereas in the second part, we report experimental results on Mg doping. Several nitrogen precursors have been used for the growth of GaN in MOVPE. To produce active species from N_2 or NH_3, a remote Plasma Enhanced Chemical Vapour Deposition (RPECVD) process has been implemented. In addition, nitrogen organic precursors, triethylamine and t-butylamine were also used. To accurately control the critical parameters of the MOVPE of GaN, we have implemented a laser reflectometry, which allows a real time in situ monitoring of the different steps of the growth. $MeCp_2Mg$ was used as Mg precursor for the p doping study. The dependence on the partial pressure of Mg precursor of dopant incorporation, electrical activity and growth rate are reported.

1. Introduction

Because GaN single crystals of suitable size are not presently available, the epitaxy of GaN should be made on foreign substrates. Sapphire, 6H-SiC, $MgAl_2O_4$, GaAs and Si are commonly used, recently new substrates with closer lattice parameters have been reported, e.g. $LiAlO_2$ and $LiGaO_2$ [1]. In the present paper sapphire (0001) oriented substrates have proven to lead to high quality GaN epilayers. However, since the lattice mismatch between GaN and sapphire is 0.14, appropriate nucleation layers are of critical importance. Presently, NH_3 is the most widely nitrogen precursor used for the growth of GaN but the requirement of high temperatures for the epitaxial growth leads to a high NH_3 partial pressure to avoid nitrogen loss during the growth and very high V/III ratio are to be used. Other potential nitrogen source have been considered [2], but neither these nitrogen precursors, nor “ single source » adducts have produced high quality GaN yet.

2. Experimental

GaN epilayers were grown in atmospheric growth chambers. In addition to the MO (TMGa, TMAl, $MeCp_2Mg$), t-butylamine $tBuNH_2$, triethylamine $N(C_2H_5)_3$ and hydrides lines, the reactors are equipped with an *in situ* control of the growth by laser reflectometry and a microwave generator to produce plasma for the decomposition of NH_3 or N_2. Beside NH_3 standard pyrolysis, we used this plasma assistance and also the two organic nitrogen precursors mentioned above to grow epitaxial structures with the same design. Prior to the deposition of a 2-3 µm GaN layer at a temperature in the range 1000 to 1080°C, a 250 nm thick GaN buffer is first deposited at 600°C. The carrier gas is nitrogen except for the growth of GaN with t-butylamine where a mixture H_2-N_2 was tested.

We have installed an in situ real time control of the growth process based on laser reflectometry (LR). The experimental set up involves an incident He-Ne beam at 632.8 nm mechanically modulated and a detection of the reflected intensity with a synchronous demodulator. For the particular AlN, GaN and sapphire material combination,

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presenting large refractive index steps and being transparent, some informations of outmost importance such as growth rate, surface smoothness, thicknesses and switching times are provided by LR in a straightforward way. During the growth of a nitride layer, the reflected light intensity follows a periodic function, the period of which is given in the case of normal incidence by $\tau= \lambda/2nV_G$ where λ is the wavelength of the laser, n the refractive index of the layer at the growth temperature, V_G the growth rate. Since nitrides are transparent at 632.8 nm, damping results from surface roughening and is indicative of unstatisfactory growth conditions. A typical recording of the reflectivity signal during an epitaxial growth of GaN on sapphire is given in Figure 1. This figure is an illustration of the real time access: the growth rate is significantly decreased from 2.5 μm/h down to 1.6 μm/h by the only fact of introducing the Mg precursor in the vapour phase.

3. Alternative nitrogen sources

Before reporting about alternative N sources, we briefly mention the state of the GaN quality that we obtained in standard process with NH_3 to establish a reference for comparison with the materials obtained with less common N sources. Using NH_3 and with an appropriate GaN buffer layer, high quality GaN layers were grown on sapphire having the following characteristics: μ_{300K}= 400cm^2/V.s and n=5.10^{16}cm^{-3}. Photoluminescence (PL) performed at 9K shows peaks having a FWHM of about 4 meV. On the best samples, the free excitons X_A, X_B and X_C are resolved in both PL and reflectivity spectra [3]. The microstructural analysis of the nucleation layer together with its thermal evolution are described in details in [4], [5], [6], [7], [8], [9], [10], [11], [12].

3.1. Plasma Activated sources

Both NH_3 and N_2 4.5 GHz microwave-plasma activated (P.A.) have been used to produce GaN epitaxial layers. PA species are introduced in the reactor by a separated entrance to avoid parasitic reactions with metalorganic compounds. The total pressure was 300 Pa and the growth sequence was similar to that used for NH_3 standard pyrolysis as described above. In the case of PA-N_2, the N concentration [N] was measured by recording the luminescence of the reaction N+NO versus the flow rate of NO introduced in the reaction chamber. [N]/[N_2] values of about 1% have been achieved with 500 W microwave input. This remote plasma source leads to growth rates of 0.7 μm/h. The photoluminescence spectra measured at 9K for GaN samples grown with PA-N_2 and PA-NH_3 respectively as nitrogen precursor show that the near band edge transitions are almost quenched. Conversely the recombination on donor-acceptor pairs are very strong in samples grown with PA-N_2. Zinc Blende GaN phase luminescence is dominating in the spectrum of the sample grown with PA-NH_3. The electrical properties was rather poor particularly in the PA-NH_3 grown GaN. We suspect that ionised H species produced by the NH_3 breaking react strongly with the quartz chamber and introduce both oxygen and silicon in the layer. At this point, it must be pointed out that, so far, NH_3 produces the best quality GaN layers.

3.2. Alternative nitrogen precursors

$N(CH_3)_3$ as a precursor did not produce GaN epitaxial layers. Deposition using this precursor results in Ga droplets. However, in the first experiments [2], only low V/III ratio were achievable, using higher ratio may produce GaN.

Among alternative nitrogen organic molecules, t-butylamine has been reported to be an efficient precursor for nitrogen doping of II-VI grown by MOVPE. t-butylamine is liquid at room temperature. The growth process for the deposition of GaN from $Ga(CH_3)_3$ and t-butylamine was basically similar to that of GaN from NH_3. Since growth using NH_3 has proven to produce better quality GaN under nitrogen carrier gas and high V/III ratio, we use V/III ratios ranging from 100 to 200. This latter value is limited by the mass-flow controller. The carrier gas was either pure hydrogen or pure nitrogen or even a 1 to 1 mixture of H_2 and N_2. Whatever the growth conditions, composition of the carrier gas, V/III ratio, temperature, GaN was not deposited. This was somehow unexpected since t-butylamine has been reported to produce p-doping in the II-VI's. Scanning Electron Analysis (in the EDX mode) reveals that the composition of the layer was mostly carbon. A thermodynamic analysis was carried out to try to explain these features even though kinetics play also a determinant role. Starting from the composition of the vapour phase used in the growth experiments, we evaluate the composition of the phases in equilibrium with the gas phase as a function of temperature by standard minimisation of the free enthalpy of the system. According to these theoretical results, it appears that GaN can not be grown above 900K in pure H_2, as already observed in calculations using NH_3. Unfortunately, under pure nitrogen, carbon is the most likely solid to be deposited. On this thermodynamic basis,

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the observed results can be understood [12]. This rules out the use of this precursor for the deposition of GaN.

4. GaN doping with magnesium

4.1. Incorporation of Mg in the GaN lattice

Only GaN grown with standard NH_3 process is concerned in this part devoted to doping with magnesium. Two precursors are available : Cp_2Mg or $MeCp_2Mg$. We used the latter one in our experiments since it has the lowest melting point and has the highest equilibrium partial pressure though Cp_2Mg is more commonly used. Figure 2 shows the Mg concentration in the lattice vs. the relative molar concentration in the vapour phase for layers grown at 1080°C with a V/III ratio of 2500 and a TMGa partial pressure of 10^{-4} Atm. These values are obtained by SIMS analysis using a Mg-implanted sample as reference. Samples grown in the same conditions exhibit very reproducible Mg profiles. $MeCp_2Mg$ is therefore a specie as suitable as Cp_2Mg for Mg doping. The fraction **k** of incorporated Mg atoms is about 10^{-2} at this temperature. A similar value was reported for Zn doping of GaN at lower temperature (950°C) on (0001) sapphire [13]. It should noticed from Figure 2 that the saturation regime, which could be due either to the Mg solubility limit or simply to the too high flow in the $MeCp_2Mg$ bubbler, is not yet reached and we expect to obtain Mg concentrations well above $10^{20}cm^{-3}$. Mg incorporation dependence on temperature has been investigated by SIMS analysis on samples grown at 1050°C from which we deduced a value for **k** of only 10^{-3}. Mg incorporation efficiency is therefore a strongly increasing function of the growth temperature. Another striking feature is illustrated on Figure 3 which schemes the growth rate dependence on the Mg partial pressure, all other growth parameters being identical. The growth rate decreases rapidly, an exponential decay is fitted through the data as guide line. This may be attributed to competition for III site occupancy between the pyrolysis by-products of TMGa (certainly $GaCH_3$) and $MeCp_2Mg$nbsp the later involving a very large carbon cycle is then expected to inhibit a larger number of surrounding sites. Whatever the Mg concentration, very optically smooth surfaces are obtained as attested by the constant envelope of the reflectivity signal recorded (see Figure 1 corresponding to a layer with $6x10^{19}$ Mg/cm^3 in the GaN lattice).

4.2. Electrical assessment

As already reported in the literature, as grown Mg doped GaN is highly resistive and no Hall measurements are achievable. Acceptors can be activated by simple thermal annealing in N_2 ambient which is assumed to allow the out diffusion of H passivating Mg in the lattice. Moreover acceptor levels associated with Mg are at 260 meV deep by luminescence (an extended study of optical properties of our Mg :GaN is in [14]) and the corresponding Hall activation energy is about 160 meV. Following [15], the ionised fraction of Mg dopant can be estimated to be in the range 2 to 5%. Though the SIMS measurements have proven that the Mg incorporation is well controlled, Hall measurement on samples after annealing in similar condition presents scattered results as shown in Figure 4. For a Mg concentration in the lattice of $4x10^{19}cm^{-3}$ corresponding to a theoretical hole concentration of ~$2x10^{18}$ cm^{-3}, we obtained measured hole concentrations between $2x10^{17}$ and $2x10^{18}$ cm^{-3}. The small mobility values of Mg doped GaN induce uncertainty on the hole concentration that can be as high as 100%. But we believe that incomplete annealing is playing the major role. As an example, the RT hole concentration of a sample annealed at 700°C for 30 minutes under N_2 at the atmospheric pressure is measured to be $6\text{-}8x10^{17}cm^{-3}$, but an extra annealing at 750°C for 10 minutes of the same sample has improved this value to $2x10^{18}cm^{-3}$.

5. Conclusions

Different potential N sources have been tested involving either plasma activation or pyrolysis of N-based organic molecules. Plasma sources allow epitaxial growth of GaN layers but their electronic quality is far beyond that of GaN deposited in NH_3 standard growth process. For both triethylamine and terbutylamine, the growth was limited by too low V/III ratio. For the particular case of terbutylamine, solid carbon deposit seems to be an intrinsic limitation to its use. Concerning Mg doping of GaN with $MeCp_2Mg$, very high and reproducible incorporation of the dopant in the lattice is obtained. P-type conduction with hole concentration in the $10^{18}cm^{-3}$ range is achieved with post growth thermal annealing at 750°C in N_2 ambient.

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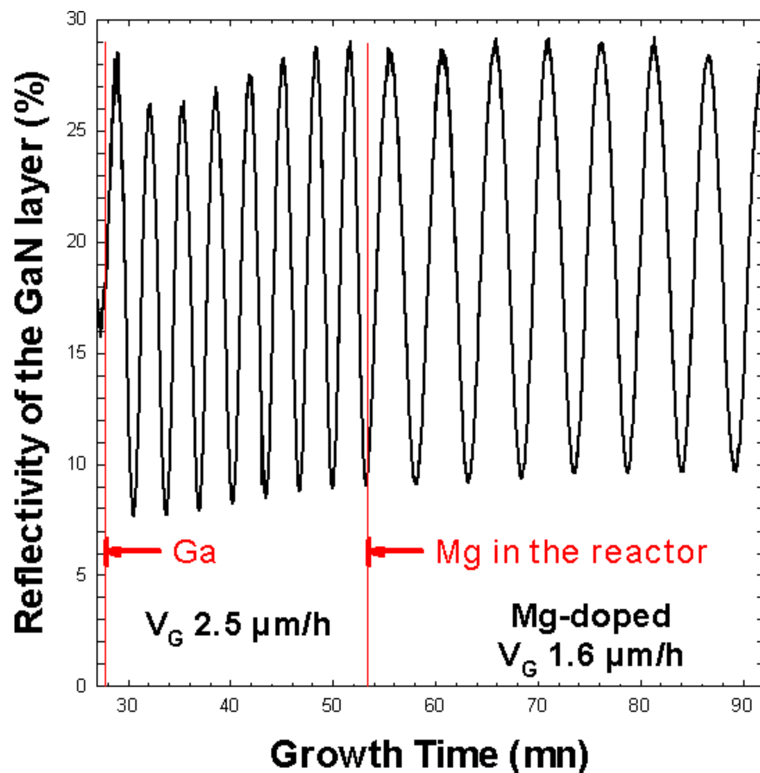

Figure 1. Reflectivity recording showing the growth rate change with Mg precursor introduction in the vapour phase.

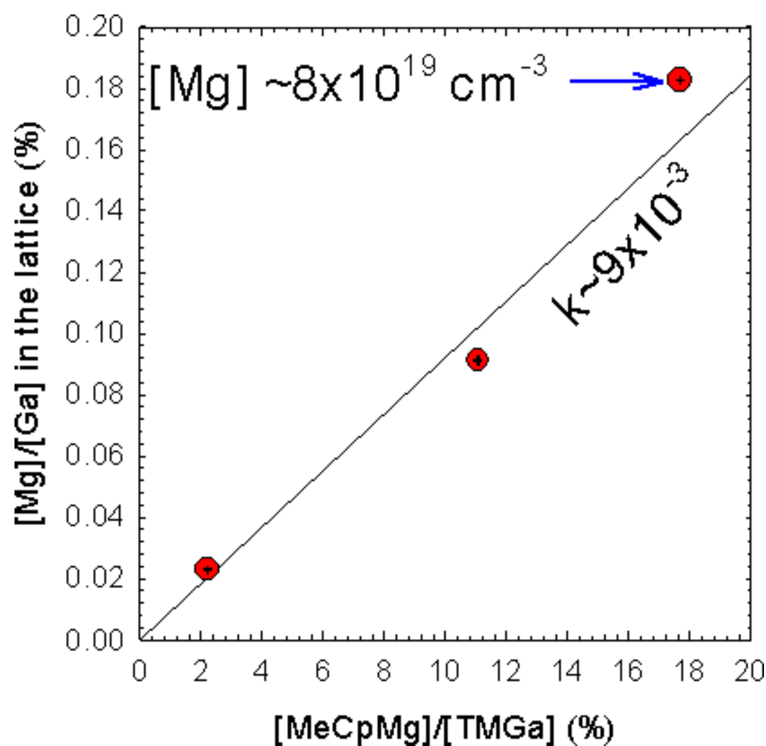

Figure 2. Incorporation of Mg in the lattice vs. relative molar composition of the vapour phase. Growth is performed at 1080°C. The fraction of Mg in the solid is only ~10^{-2} at this temperature.

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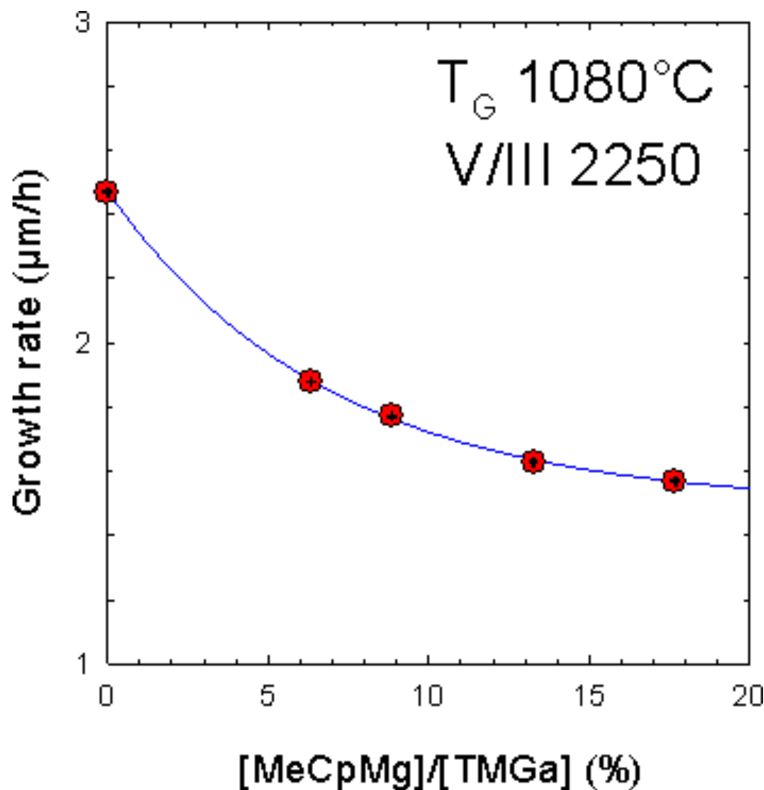

Figure 3. Growth rate dependence on Mg precursor normalised partial pressure. The continuous line is an exponential decay fit to the experimental data.

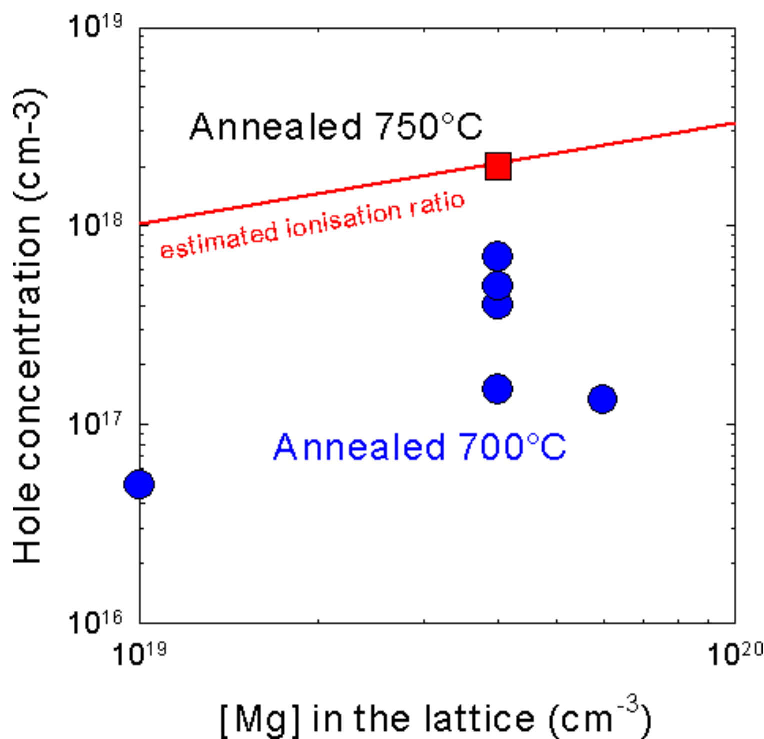

Figure 4. Hall concentration vs. Mg concentration in the lattice at room temperature. Dots are samples annealed at 700°C under N_2 ambient for 30 minutes. The square is one of the previous sample ($6x10^{17}$ cm^{-3}) that has gained a factor 2 in hole concentration by experiencing an extra annealing at 750°C for 10 minutes. The line indicates the level of hole concentration expected from the neutrality equation with an activation energy of about 160 meV.

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